

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : <b>C07C 45/50, 67/347, 69/716, 253/30, 255/17, B01J 31/28, 31/38</b>	A1	(11) International Publication Number: <b>WO 97/08123</b> (43) International Publication Date: <b>6 March 1997 (06.03.97)</b>
(21) International Application Number: <b>PCT/US96/13350</b>		(81) Designated States: CA, CN, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: <b>15 August 1996 (15.08.96)</b>		
(30) Priority Data: <b>08/519,833 25 August 1995 (25.08.95) US</b>		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(71) Applicants: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 Heerlen (NL).		
(72) Inventor: BURKE, Patrick, Michael; 4613 Talley Hill Lane, Wilmington, DE 19803-4815 (US).		
(74) Agent: DEITCH, Gerald, E.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		

(54) Title: HYDROFORMYLATION PROCESS

(57) Abstract

A hydroformylation process for the production of linear aldehydes from linear olefins, by the reaction of the olefin with hydrogen and carbon monoxide in a solvent containing a catalyst having a platinum component or palladium component, a bidentate diaryl phosphine component where the bridging group is ferrocenyl or 3 to 6 carbon atoms, and a metal promoter component.

BEST AVAILABLE COPY

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Larvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

TITLE

## HYDROFORMYLATION PROCESS

FIELD OF THE INVENTION

This invention relates to the hydroformylation of olefins to form the  
5 corresponding aldehydes.

BACKGROUND OF THE INVENTION

Botteghi et al. in Journal of Organometallic Chemistry 417 (1991) C41-C45 in an article titled "Hydroformylation of olefins catalyzed by alkene complexes of platinum(0)" disclose hydroformylation using a bidentate phosphino compound, a platinum catalyst, and an acid promoter in an organic solvent. This article notes: "..., internal double bonds are rather unreactive as shown by the hydroformylation of cyclohexene ...".

An object of the present invention is to provide a process for the hydroformylation of internally unsaturated olefins or terminally unsaturated  
15 olefins to form particular linear aldehyde products.

SUMMARY OF THE INVENTION

The present invention is a process for the preparation of linear aldehydes which comprises contacting a linear olefin, hydrogen, water, and carbon monoxide in an organic solvent containing a dissolved catalyst comprising: (a) a platinum  
20 compound free of anionic halide or palladium compound free of anionic halide, (b) a bidentate diaryl phosphine ligand where each of the aryl groups contain up to 15 carbon atoms and where the bridging group contains 3 to 6 carbon atoms or is a ferrocenyl group, and (c) a promoter selected from the group consisting of (i) a metal perfluoroalkane sulfonate where the alkane has 1 to 10 carbon atom, (ii) a  
25 metal perfluoro-betadiketonate of up to 11 carbon atoms, and (iii) a metal trifluoroacetate; where the metal in (i), (ii), and (iii) is selected from the group consisting of aluminum, scandium, nickel, zinc, yttrium, zirconium, tin, lanthanum, and lanthanide elements from praseodymium to lutecium; where the ratio of (c) to (a) is in the range of 0.5/1 to 20/1, and the ratio of (b) to (a) is in the  
30 range of 0.8/1 to 1.5/1.

Preferably the olefin contains 2 to 10 carbon atoms. One preferred olefin is 3-pentenenitrile and the linear aldehyde product is 5-formylvaleronitrile.

Another preferred olefin is a methyl pentenoate and the linear aldehyde product is methyl-5-formylvalerate.

35 The process will usually be carried out at a temperature in the range of 80 to 120°C and the carbon monoxide pressure in the range of 500 to 3000 pounds per square inch.

The present invention is also a composition comprising organic solvent containing a dissolved catalyst comprising: (a) a platinum compound free of anionic halide or palladium compound free of anionic halide, (b) a bidentate diaryl phosphine ligand where each of the aryl groups contains up to 15 carbon atoms, 5 where the bridging group contains 3 to 6 carbon atoms or is a ferrocenyl group, and (c) a promoter selected from the group consisting of (i) a metal perfluoroalkane sulfonate where the alkane has 1 to 10 carbon atoms, (ii) a metal perfluoro-betadiketonate of up to 11 carbon atoms, and (iii) a metal trifluoroacetate; where the metal in (i), (ii), and (iii) is selected from the group 10 consisting of aluminum, scandium, nickel, zinc, yttrium, zirconium, tin, lanthanum, and lanthanide elements from praseodymium to lutecium; where the ratio of (c) to (a) is in the range of 0.5/1 to 20/1, and the ratio of (b) to (a) is in the range of 0.8 to 1.5/1.

In both the process and the composition the ratio of water to metal 15 promoter is 200:1 or less.

Preferably the linear olefin contains 4 to 10 carbon atoms.

Suitable solvents include acetonitrile, adiponitrile, methylglutaronitrile, 20 dimethyladipate, valerolactone, methylisobutylketone, dimethylacetamide, dimethylformamide, methylene chloride, mixtures of one of the above nitriles and toluene, and homogeneous mixtures of the above nitriles and water. The solvent may also be an alkanol containing 1 to 6 carbon atoms, for example methanol or ethanol. In these cases the product will be the acetal of the aldehydes formed in the hydroformylation reaction. The catalysts of this invention are therefore dual functional in that they catalyze both the hydroformylation and acetalization 25 reactions simultaneously. When the process of the present invention is operated in a continuous manner, the product will be removed from the solvent and the solvent recycled, and gradually the composition of the solvent will change as more and more by-products of the reaction remain in the recycled solvent.

Preferred bidentate diaryl phosphine ferrocene ligands having the formula 30 Ar<sub>2</sub>P-Q-PAr<sub>2</sub> include: 1,1'-Bis(diphenylphosphino)ferrocene, sometimes referred to hereinafter as DPPF; 1,1'-Bis(di-m-fluorophenylphosphino)ferrocene; 1,1'-Bis(di-p-methylphenylphosphino)ferrocene; and 1,1'-Bis(diphenylphosphino)3,3'-(trimethylsilyl)ferrocene.

Preferred bidentate diaryl phosphine ligands having bridging groups of 35 3 to 6 carbon atoms include: (+)-2,3-O-Isopropylidine-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane; sometimes referred to hereinafter as DIOP; (-)-(2S,4S)-2,4-Bis(diphenylphosphino)pentane; sometimes referred to hereinafter as S,S-BDPP; 1,3-Bis(diphenylphosphino)propane; sometimes referred to

hereinafter as DPPP; (S)-(-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl sometimes referred to hereinafter as BINAP; and 1,4-Bis(diphenylphosphino)butane sometimes referred to hereinafter as DPPB.

#### DETAILED DESCRIPTION OF THE INVENTION

5 Suitable olefins for hydroformylation into linear aldehydes include:

(1) pentenoic acid esters such as 2- and 3-pentenoic acid esters where the non-pentenoic acid portion is from a hydrocarbon alcohol. The hydrocarbon alcohol may be saturated or unsaturated, aliphatic or aromatic but usually will have from 1 to 8 carbon atoms. (2) 2- and 3-pentenenitrile (3) hexene-1 and hexene-2, etc.

10 The olefin may be an internal olefin or a terminal olefin. The olefin may be substituted with other groups such as carboxyl, ester, nitrile, aldehyde, or ketone groups.

15 The organic solvent for use in the process should dissolve the platinum catalyst compound or the palladium catalyst compound, the compound to be hydroformylated, the bidentate diarylphosphine ligand, the promoter, and the product. Stated another way, the solvent should provide a homogeneous reaction mixture. Suitable solvents include acetonitrile, adiponitrile, methylglutaronitrile, dimethyladipate, caprolactone, dichloromethane, 2-butanone, propylenecarbonate, valerolactone, methylisobutylketone, methylene chloride, mixtures of one of the 20 above nitriles and toluene, and homogeneous mixtures of the above nitriles and water. When the process of the present invention is operated in a continuous manner, the product will be removed from the solvent and the solvent recycled, and gradually the composition of the solvent will change as more and more by-products of the reaction remain in the recycled solvent.

25 The platinum component or the palladium component of the catalyst must be free of anionic halide but may contain covalent halide, e.g., fluorinated beta-diketonate. Platinum(II) or palladium(II) beta-diketonate, platinum(II) or palladium(II) carboxylates, and platinum or palladium complexes such as Pt(cyclooctadiene)2 or Pd(cyclooctadiene)2 may be the catalyst component.

30 The promoter is selected from the group consisting of: (i) a metal perfluoroalkane sulfonate where the alkane has 1 to 10 carbon atoms, (ii) a metal perfluoro-beta-diketonate of up to 11 carbon atoms, and (iii) a metal trifluoroacetate; where the metal in (i), (ii), and (iii) is selected from the group consisting of aluminum, scandium, nickel, zinc, yttrium, zirconium, tin, lanthanum, and 35 lanthanide elements from praseodymium to lutecium. Specific promoters from the above groups that are effective are: lanthanum, or dysprosium, or neodymium, or ytterbium trifluoromethanesulfonate; neodymium, or zirconium, or ytterbium, or scandium, or praseodymium, or lanthanum, hexafluoroacetylacetones.

The bidentate diaryl phosphine ligand having the formula Ar<sub>2</sub>P-Q-PAr<sub>2</sub> where Q is a ferrocenyl group and each of the Ar groups contain 6 to 15 carbon atoms include such compounds as 1,1'-Bis(diphenylphosphino)ferrocene; 1,1'-Bis(di-m-fluorophenylphosphino)ferrocene; 1,1'-Bis(di-p-methylphenylphosphino)ferrocene; 1,1'-Bis(diphenylphosphino)3,3'-trimethylsilyl)ferrocene; 1,1'-Bis(di-p-trifluoromethylphenylphosphino)ferrocene and 1,1'-Bis(di-3,5-(bis(trifluoromethyl)phenylphosphino)ferrocene, and where Q is a bridging group containing 3 to 6 carbon atoms (+)2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane; (-)-(2S,4S)-2,4-Bis(diphenylphosphino)pentane; 1,3-Bis(diphenylphosphino)propane; (S)-(-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl.

#### EXAMPLE 1

##### M3P Hydroformylation with Pt(AcAc)<sub>2</sub>/DPPF/La(OSO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>

A 25 ml glass lined shaker tube was charged with 5 ml of a solution containing 11.4 g (100 mmole) methyl-3-pentenoate (M3P), 0.393 g (1.0 mmole) platinum(II) acetylacetone (Pt(AcAc)<sub>2</sub>), 0.70 g (1.26 mmole) 1,1'-Bis(diphenylphosphino)ferrocene (DPPF), 2.93 g (5 mmole) lanthanum trifluoromethane sulfonate La(OSO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>, 0.2 g (11 mmole) water and 1.00 g o-dichlorobenzene (ODCB, internal GC standard) in 100 ml of a 4:1 mixture of toluene and acetonitrile. The solution contained 0.05 mg-atom Pt and a Pt(AcAc)<sub>2</sub>/DPPF/La(OSO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>/H<sub>2</sub>O mole ratio of 1:1.26:5:11.

The shaker tube was freed from air by purging first with 100 psi nitrogen (twice) and then with 1:1 CO/H<sub>2</sub> (twice). The tube was then pressurized to 700 psi CO/H<sub>2</sub> and heated 100°C over 30 minutes. The pressure was then adjusted with 1:1 CO/H<sub>2</sub> to 1000 psi at 100°C. The temperature was maintained at 100°C with shaker agitation for 2 hours. The heat was shut off and the shaker tube was allowed to cool to 25-35°C. The excess CO/H<sub>2</sub> was vented and the product was analyzed for methyl esters and formylvalerates on a capillary GC column. The analysis showed (in g/100 ml):

	<u>Conversion</u>	<u>21.4%</u>
	<u>Selectivities</u>	
	Methyl-5-formylvalerate (M5FV)	82.8
	Methyl-4-formylvalerate (M4FV)	6.1
35	Methyl-3-formylvalerate (M3FV)	0.8
	Methyl-4-pentenoate (M4P)	3.0
	Cis-methyl-2-pentenoate (CM2P)	0.8
	Trans-methyl-2-pentenoate (TM2P)	3.7
	Methylvalerate (MV)	2.9

Accounting (sum of all analyzed products and starting material): 99%

The yield to the desired product, methyl-5-formylvalerate (M5FV), is

5 82.8% at 21% conversion and the linearity (100\* M5FV/(M5FV+M4FV+M3FV)) is 92.3%.

The example illustrates the very high selectivity to linear aldehyde from an internal olefin that may be obtained with the catalyst of this invention.

In the following examples the products were analyzed in the same way but 10 the results are expressed in summary form as combined conversion of M3P and M4P ("Conv"), Selectivity to methyl-5-formylvalerate ("Sel"), linearity and product accounting ("Acctg").

#### EXAMPLES 2-9

##### 1. Promotion with Metal Trifluoromethanesulfonates

15 a. DPPF Ligand and Various Metal Trifluoromethanesulfonates  
M3P Hydroformylation with Pt(AcAc)<sub>2</sub>/DPPF/M(OSO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>

The experiment in Example 1 was repeated except that the lanthanum trifluoromethanesulfonate was replaced with an equivalent amount of other metal trifluoromethanesulfonates and the mole ratios of trifluoromethanesulfonate to 20 platinum and of water to metal trifluoromethanesulfonate were varied. The results are shown in Table 1.

TABLE 1

Ex.	Metal	M/Pt	H <sub>2</sub> O/M	Conv	Sel	Lin	Acctg
2	La	5	0	35	84	94	99
3	La	5	3	54	81	93	96
4	La	5	1	51	81	94	98
5	Dy	5	0	64	56	80	89
6	Dy	5	1	79	53	80	87
7	Dy	1	0	14.3	78	91	96
8	Nd	5	0	82	52	80	95
9	Yb	1	2	24.5	79	91.0	95.3

These examples show that the hydroformylation reaction may be promoted 25 with a variety of metal trifluoromethanesulfonates.

EXAMPLES 10-17b. Lanthanum Trifluoromethanesulfonate and  
Various Bidentate Phosphine LigandsM3P Hydroformylation with  $\text{Pt}(\text{AcAc})_2/\text{LIGAND/La}(\text{OSO}_3\text{CF}_3)_3$ 

5 The experiment in Example 1 was repeated except that the DPPF ligand was replaced with an equivalent amount of other bidentate phosphine ligands and the water to metal ratio was varied. The results are shown in Table 2.

TABLE 2

Ex.	Ligand	M/Pt	H <sub>2</sub> O/M	Conv	Sel	Lin	Acctg
10	DIOP	5	1	29	72	83	98
11	DIOP	5	0	26	73	85	97
12	(S,S)-BDPP	5	0	58	61	85	85
13	DPPP	5	0	13	44	62	101
14	BINAP	5	0	1.3	37	89	102
15	DPPB	5	0	25	61	70	98
16	DPPB	5	1	24	69	80	97
17	DPPB	5	3	15	74	85	100

10 DIOP = (+)-2,3-O-Isopropylidine-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane  
(S,S)-BDPP = (-)-(2S,4S)-2,4-Bis(diphenylphosphino)pentane  
DPPP = 1,3-Bis(diphenylphosphino)propane  
BINAP = (S)-(-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl  
15 DPPB = 1,3-Bis(diphenylphosphino)butane

These examples show that good selectivity can be obtained with a variety of bidentate phosphine ligands containing a 3 or 4 carbon chain between the phosphorus atoms.

EXAMPLES 18-2820 2. Promotion with Metal Hexafluoroacetylacetones

a. DPPF Ligand and Various Metal Hexafluoroacetylacetones  
M3P Hydroformylation with  $\text{Pt}(\text{AcAc})_2/\text{DPPF/M(HFAA)}_n$

The experiment in Example 1 was repeated except that the lanthanum triflate was replaced with an equivalent amount of various metal

25 hexafluoroacetylacetones and the mole ratios of metal HFAA to platinum and of water to metal HFAA were varied. The results are shown in Table 3.

TABLE 3

Ex.	HFAA	M/Pt	H <sub>2</sub> O/M	Conv	Sel	Lin	Acctg
18	Nd(III)	2	2	13	80	92	99
19	Nd(III)	5	2	33	82	92	94
20	Nd(III)	10	2	42	82	91	91
21	Zr(IV)	5	2	29	82	93	98
22	Y(III)	5	2	16	80	91	95
23	Y(III)	5	0	17	69	87	100
24	Sc(III)	5	2	61	71	93	70
25	Sc(III)	5	0	51	74	93	75
26	Pr(III)	5	3	30	80	93	90
27	Zn(II)	5	2	16	76	92	101
28	Al(III)	5	2	24	61	91	103

DPPF = 1,1'-Bis(diphenylphosphino)ferrocene

These examples show that a wide variety of metal hexafluoroacetyl-acetonates are active promoters for the hydroformylation.

5

#### EXAMPLE 29

##### Activity Demonstration: Hydroformylation of M3P with Pt(AcAc)<sub>2</sub>/DPPF/La(OTf)<sub>3</sub> at 100°C and 1000 psi

A 160 ml mechanically stirred zirconium autoclave was flushed with nitrogen and then with 600 psi of 1:1 CO/H<sub>2</sub>. It was then charged with a solution of 0.35 g (0.62 mmole) DPPF ligand, 1.46 g (2.5 mmole) lanthanum triflate promoter, 0.13 g (7.5 mmole) water and 32.4 g 4:1 toluene/acetonitrile solvent. The autoclave was pressured with 1:1 CO/H<sub>2</sub> to 700 psi and heated to 100°C. The reaction was initiated by adding a solution of 5.0 grams (44 mmole) of M3P and 0.5 g ODCB internal GC standard in 10 g 4:1 toluene/acetonitrile solvent. The pressure was immediately adjusted with CO/H<sub>2</sub> to 1000 psi at 100°C. CO/H<sub>2</sub> was continuously fed to the autoclave from a reservoir so as to maintain the total pressure constant at 1000 psi. Samples were removed at intervals for GC analysis. The reaction was allowed to run for a total of 3 hours after which it was cooled to 20°C. The excess CO/H<sub>2</sub> was vented through a control valve and the product was discharged.

The samples from the reactor were analyzed on a 30 m Carbowax capillary GC column. The results are shown below.

Time (Min)	Conversion (%)	Selectivity (% M5FV)	Linearity (%)
15	8.2	91.7	93.6
60	15.6	90.2	93.7
120	30.2	89.1	92.5
180	44.4	89.1	92.5
240	55.2	88.9	92.6

The first order rate constant is 0.2/Hr and the turnover frequency from this rate is 72 moles/mole Rh/Hr.

5 This example illustrates that the reaction is first order in pentenoate to at least 50% conversion.

#### EXAMPLES 30-36

##### Hydroformylation of Hexenes with Pt(AcAc)2/DPPF/+ Promoter

The experiment in Example 1 was repeated except that the M3P was replaced by Hexene-1, trans-Hexene-2 or trans-Hexene-3, the promoter was varied 10 and the mole ratio of water to promoter was varied. The results are shown in Table 4.

TABLE 4

Ex.	BH Ex. No.	Olefin	Promoter (P)	H <sub>2</sub> O/P	Conv	Sel to n- Heptanal
30	112-1b	1-Hexene	La(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	10	56	93
31	112-2b	1-Hexene	Nd(HFAA)3	10	27	85
32	112-4b	1-Hexene	Dy(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	0	10	71
33	112-1c	t-2-Hexene	La(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	10	6.6	86
34	112-2d	t-3-Hexene	Nd(HFAA)3	10	18	86
35	112-2e	t-2-Hexene	Nd(HFAA)3	10	23	89
36	112-4d	t-3-Hexene	Dy(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	0	23	84

These examples illustrate that high selectivity can be obtained with both 15 terminal and internal olefins with the catalyst of this invention.

#### EXAMPLES 37-42

##### Hydroformylation of Pentenoic Acids with Pt(AcAc)2 + Ligand + Promoter

The experiment in Example 1 was repeated except that the M3P was replaced by 3-pentenoic acid (3PA) or 4-pentenoic acid (4PA) and both the 20 promoter and phosphorus ligand were varied and the reaction was allowed to run for 4 hours. The results are shown in Table 5.

TABLE 5

Ex.	Olefin	Ligand	Promoter (P)	H <sub>2</sub> O/P	Conv	Sel to 5FVA	Lin
37	3PA	DPPF	La(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	10	72	51	72
38	3PA	DPPF	Nd(HFAA)3	10	87	83	89
39	3PA	DIOP	Nd(HFAA)3	10	87	81	86
40	3PA	DIOP	La(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	10	42	44	75
41	4PA	DPPF	La(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	10	70	54	74
42	4PA	DPPB	La(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	10	68	21	76

These experiments illustrate the application of the catalyst to olefins that contain a carboxylic acid function.

#### EXAMPLE 43

5 The experiment in Example 1 was repeated except that the M3P was replaced by 3-pentenenitrile (6M Concentration) and the solvent was toluene. After 6 hours the conversion of 3PN was 6.8%, the selectivity to 5-formylvaleronitrile was 45% and the linearity was 88.4%.

10 This example illustrates the applicability of the catalyst to internal olefins containing a nitrile function.

#### EXAMPLES 44-50

##### Hydroformylation of M3P was Pt(AcAc)<sub>2</sub> + DPPF + Metal Trifluoroacetate

15 The experiment in Example 1 was repeated except that the promoter was a trifluoroacetate and the water/promoter and promoter/Pt ratios were varied. The results are shown in Table 6.

TABLE 6

Ex.	BH Ex. No.	Promoter (P)	P/Pt	H <sub>2</sub> O/P	Conv	Sel to M5FV	Lin
44	123-1a	Y(OCOCF <sub>3</sub> ) <sub>3</sub>	5	0	8.8	80	92
45	124-4b	Y(OCOCF <sub>3</sub> ) <sub>3</sub>	10	0	38	67	89
46	125-2a	Y(OCOCF <sub>3</sub> ) <sub>3</sub>	10	2	28	52	86
47	134-1b	La(OCOCF <sub>3</sub> ) <sub>3</sub>	5	0	35	83	92
48	134-1d	Dy(OCOCF <sub>3</sub> ) <sub>3</sub>	5	0	34	67	89
		3					
49	134-2b	Er(OCOCF <sub>3</sub> ) <sub>3</sub>	5	0	37	78	90
50	134-2d	Yb(OCOCF <sub>3</sub> ) <sub>3</sub>	5	0	34	81	91

3

These examples illustrate the activity of trifluoroacetates of a variety of metals for the hydroformylation reaction.

EXAMPLE 51Hydroformylation of M3P with Pd(AcAc)2 + DPPP + La(OSO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>  
in Dimethylacetamide (DMAc) Solvent

A 25 ml glass lined shaker tube was charged with 5 ml of a solution  
 5 containing 11.4 g (100 mmole) methyl-3-pentenoate (M3P), 0.304 g (1.0 mmole) palladium(II) acetylacetonate (Pd(AcAc)2), 0.52 g (1.26 mmole), 1,3'-bis(diphenylphosphino)propane, 2.93 g (5 mmoles) lanthanum trifluoromethane sulfonate (La(OSO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>) and 1.00 g o-dichlorobenzene (ODCB, internal GC standard) in 100 ml of dimethylacetamide. The solution  
 10 contained 0.05 mg-atom Pd and a Pd(AcAc)2/DPPP/La(OSO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub> mole ratio of 1:1.26:5.

The shaker tube was freed from air by pressurizing and depressurizing first with 100 psi nitrogen (twice) and then with 1:1 CO/H<sub>2</sub> (twice). The tube was then pressurized to 700 psi CO/H<sub>2</sub> and heated 100°C over 30 minutes. The pressure  
 15 was then adjusted with 1:1 CO/H<sub>2</sub> to 1000 psi at 100°C. The temperature was maintained at 100°C with shaker agitation for 2 hours. The heat was shut off and the shaker tube was allowed to cool to 25-35°C. The excess CO/H<sub>2</sub> was vented and the product was analyzed for methyl esters and formylvalerates on a capillary GC column. The results are shown in Table 7.

EXAMPLE 52Hydroformylation of M3P with Pd(AcAc)2 + DPPP + La(OSO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>  
in Dimethylacetamide (DMAc) Solvent

The experiment in Example 51 was repeated except that the M3P was replaced with M4P. The result are summarized in Table 7.

EXAMPLES 53-56Hydroformylation of M3P with Pd(AcAc)2 + Ligand + Promoter  
in Dimethylacetamide (DMAc) Solvent

The experiment in Example 51 was repeated except that ligand and promoter were varied. The results are summarized in Table 7.

Ex.	Olefin	Ligand	Promoter	Conv	Sel to 5FVA	Lin
51	M3P	DPPP	La(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	15	51	.60
52	M4P	DPPP	La(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	28	64	67
53	M3P	S,S-BDPP	La(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	20	40	63
54	M3P	DPPP	Dy(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	10	53	60
55	M3P	DPPP	Al(HFAA)3	7.3	42	52
56	M3P	DPPP	Sc(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	8.9	51	61

The above examples illustrate the application of the metal trifluoromethane sulfonate and hexafluoroacetylacetone promoters for the activation of palladium catalysts in a polar aprotic solvent.

5

### EXAMPLES 57-62

#### Hydroformylation of M3P with (DPPF)PtC<sub>2</sub>H<sub>4</sub> + CPPF + Promoter

The experiment in Example 1 was repeated except that the platinum catalyst precursor was (DPPF)PtC<sub>2</sub>H<sub>4</sub>, additional DPPF was added to maintain the 1.26/1 ligand/Pt ratio and the promoter and water were varied. The results are 10 summarized in Table 8.

TABLE 8

Ex	Promoter (P)	(P)/P+	H <sub>2</sub> O/(P)	Conv	Sel to M5FV	Lin
57	La(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	2	0	19	86	93
58	Nd(HFAA) <sub>3</sub>	2	0	31	84	93
59	Sc(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	1	0	75	47	80
60	La(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	1	2	14	85	92
61	La(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	1	4	22	86	93
62	La(OSO <sub>3</sub> CF <sub>3</sub> ) <sub>3</sub>	1	8	28	86	93

These examples show that the ligand may be incorporated into the Pt precursor, that the initial oxidation state of the catalyst may be zero and that 15 catalyst activity increases as the ratio of triflate to Pt increases.

CLAIMS

1. A process for the preparation of linear aldehyde which comprises contacting a linear olefin, hydrogen, water, and carbon monoxide in a solvent containing a dissolved catalyst comprising: (a) a platinum or palladium compound free of anionic halide, (b) a bidentate diaryl phosphine ligand where each of the aryl groups contain up to 15 carbon atoms and where the bridging group contains 3 to 6 carbon atoms or is a ferrocenyl group, and (c) a promoter selected from the group consisting of (i) a metal perfluoroalkane sulfonate where the alkane has 1 to 10 carbon atoms, (ii) a metal perfluoro-betadiketonate of up to 11 carbon atoms, and (iii) is selected from the group consisting of aluminum, scandium, nickel, zinc, yttrium, zirconium, tin, lanthanum, and lanthanide elements from praseodymium to lutecium; where the ratio of (c) to (a) is in the range of 0.5/1 to 20/1, and the ratio of (b) to (a) is in the range of 0.8/1 to 1.5/1.
2. The process of Claim 1 in which the olefin contains 2 to 10 carbon atoms.
3. The process of Claim 1 in which the olefin is 3-pentenenitrile and the linear aldehyde is 5-formylvaleronitrile.
4. The process of Claim 1 in which the olefin is a methyl pentenoate and the linear aldehyde is methyl-5-formylvalerate.
5. The process of Claim 1 in which the solvent is selected from the group consisting of acetonitrile, dimethyladipate, dimethylacetamide, dimethyl-formamide, valerolactone, methylisobutylketone, methylene chloride, toluene, mixtures of a nitrile and toluene, and mixtures of a nitrile and water.
6. The process of Claim 1 in which the temperature is in the range of 80 to 120°C and the carbon monoxide pressure is in the range of 500 to 3000 pounds per square inch.
7. A composition comprising solvent containing a dissolved catalyst comprising: (a) a platinum or palladium compound free of anionic halide, (b) a bidentate diaryl phosphine ligand where each of the aryl groups containing up to 15 carbon atoms, where the bridging group contains 3 to 6 carbon atoms or is a ferrocenyl group, and (c) a promoter selected from the group consisting of (i) a metal perfluoroalkane sulfonate where the alkane has 1 to 10 carbon atoms, (ii) a metal perfluoro-betadiketonate of up to 11 carbon atoms, and (iii) a metal trifluoroacetate; where the metal is (i), (ii), and (iii) is selected from the group consisting of aluminum, scandium, nickel, zinc, yttrium, zirconium, tin, lanthanum, and lanthanide elements from praseodymium to lutecium; where the ratio of (c) to (a) is in the range of 0.5/1 to 20/1, and the ratio of (b) to (a) is in the range of 0.8 to 1.5/1.

8. The composition of Claim 7 in which the solvent is selected from the group consisting of acetonitrile, dimethyladipate, dimethylacetamide, dimethylformamide, valerolactone, methylisobutylketone, methylene chloride, toluene, mixtures of a nitrile and toluene, and mixtures of a nitrile and water.
- 5 9. The process of Claim 1 in which the ratio of water to metal promoter is within the range of 1:1 to 200:1.
10. The process of Claim 1 in which the olefin is selected from the group consisting of methylpentenoate and a pentenenitrile.
11. The process of Claim 1 in which the carbon monoxide partial pressure is in the range of 500 to 3000 pounds per square inch.

# INTERNATIONAL SEARCH REPORT

1  mail Application No  
PCT/US 96/13350

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 C07C45/50 C07C67/347 C07C69/716 C07C253/30 C07C255/17  
 B01J31/28 B01J31/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 18783 A (DSM NV ) 13 July 1995 see the whole document ---	1-6
A	EP 0 220 767 A (SHELL INT RESEARCH) 6 May 1987 see the whole document ---	1
A	EP 0 495 547 A (SHELL INT RESEARCH) 22 July 1992 see the whole document ---	1
A	GB 2 256 641 A (SHELL INT RESEARCH) 16 December 1992 see the whole document -----	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

2

Date of the actual completion of the international search

11 December 1996

Date of mailing of the international search report

20.12.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Bonnevalle, E

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Final Application No  
PCT/US 96/13350

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9518783	13-07-95	BE-A-	1008020	12-12-95
		BE-A-	1008019	12-12-95
		CA-A-	2180663	13-07-95
		EP-A-	0742788	20-11-96
		AU-A-	1327195	01-08-95
		WO-A-	9519331	20-07-95
EP-A-0220767	06-05-87	JP-A-	62106038	16-05-87
		US-A-	4731487	15-03-88
EP-A-0495547	22-07-92	CA-A-	2059233	16-07-92
		CA-A-	2059236	16-07-92
		CN-A-	1063277	05-08-92
		DE-D-	69204691	19-10-95
		DE-T-	69204691	11-04-96
		DE-D-	69210054	30-05-96
		EP-A-	0495548	22-07-92
		ES-T-	2088082	01-08-96
		ES-T-	2077337	16-11-95
		JP-A-	5058949	09-03-93
		JP-A-	4334340	20-11-92
		US-A-	5210280	11-05-93
GB-A-2256641	16-12-92	NONE		

**THIS PAGE BLANK (USPTO)**

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record.**

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**